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(54) IMAGE-FORMING MATERIAL CONTAINING A MOLYBDENUM OR TUNGSTEN POLYACID AND PROCESS USING SAID MATERIAL

(71) We, DAI NIPPON INSATSU KABUSHIKI KAISHA, a company organized and existing under the Laws of Japan, of 12, Kaga-cho 1-chome, Ichigaya, Shinjuku-ku, Tokyo-to, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to techniques in forming visible pictures or images through the use of so-called nonsilver photosensitive materials or photosensitive materials comprising compounds other than silver salts. More particularly, the invention relates to a process for forming visible pictures or images (hereinafter referred to as "images") of excellent contrast with high sensitivity by treating an image forming agent comprising a polyacid of molybdenum or tungsten or its salt or complex and relates also to an image-forming material for this process.

It is known that heteropolyacids molybdenum and tungsten as mentioned above, such as phosphomolybdic acid, for example, are reduced by light or heat to develop colors ranging from blue to black. Furthermore, attempts have been and are being made to utilize this phenomenon for formation of images through the use of flash light. One known technique for this purpose comprises placing on a reflecting original a heat-sensitive material formed by applying phosphomolybdic acid, for example, as a coating on a transparent substrate and projecting a flash light through this heat-sensitive material to the reflecting original and imparting heat rays from the black parts of the reflecting original as radiant heat to the heat-sensitive material thereby to impart an image to the heat-sensitive material. (USP 2,980,551).

In the practice of this method, how-

ever, a number of difficulties are encountered. For example, the resolution or resolving power decreases because of heat diffusion toward the periphery of the image, and only materials which are transparent and, moreover, have low heat conductivity can be used for the support.

In addition, the specifications of British Patent No. 1,008,537 and United States Patent 3,285,746 both disclose the projecting of intense light rays having an energy exceeding a certain threshold value onto a film consisting of a solid solution comprising a polyacid such as phosphomolybdic acid or silicotungstic acid and a polyvinyl alcohol/acetate copolymer or polyvinyl butyral thereby to cause the film to become opaque. From the teaching of these patented inventions, it is understood that the above mentioned material can be used as a photographic material capable of producing an image when irradiated by intense, image-wise light rays. However, since it is necessary to project continuously image light rays of a high intensity required for this process (i.e., because of low sensitivity), the utility of the material as a photographic material must be judged to be low.

As a result of our studies on the coloring or color-developing phenomenon of compounds such as phosphomolybdic acid, we have discovered that this coloring includes two process stages.

More specifically, in the first stage, phosphomolybdic acid is reduced and temporarily undergoes a weak coloring. In the case where this coloring is extremely weak, the image may be a latent image. This primary coloring is attained by the reduction of phosphomolybdic acid as was known heretofore, and for this purpose, a method of irradiating with ultraviolet rays the phosphomolybdic acid coexisting with a reducing agent or a method of bringing

a reducing agent in contact with the phosphomolybdic acid, can be resorted to.

In the second stage, the phosphomolybdic acid which has undergone the above described primary coloring further absorbs light and becomes of dark or black color. A noteworthy point is that this second stage cannot be caused to progress by irradiation with only ultraviolet rays but can be caused to progress only by using light rays having wavelengths longer than the ultraviolet region (visible and infrared rays). While light having a long wavelength of this character has a color darkening effect with respect to phosphomolybdic acid which has undergone the primary coloring, it has no effect whatsoever on phosphomolybdic acid which has not undergone the primary coloring. This property of phosphomolybdic acid is not limited to only this acid but is common to polyacids of molybdenum and tungsten and to salts and complexes thereof as described hereinafter.

On the basis of the above findings, we have carried out further studies. As a result, we have developed an improved photosensitive material using non-silver materials, and image-forming process using the material.

According to the present invention there is provided an image-forming material comprising: a substrate; an image-forming layer provided on or absorbed in at least one surface of the substrate and containing an image-forming agent selected from polyacids of molybdenum and tungsten and salts and complexes of these polyacids; and a transparent polymer film provided on the image-forming layer, at least one of the image-forming layer and the transparent polymer film containing a reducing agent capable of reducing the image-forming agent when irradiated with ultra-violet radiation.

The present invention also provides an image-forming process comprising: 1) subjecting an image-forming material of the invention to image-wise exposure to ultraviolet radiation to cause reduction of the image-forming agent and to cause it to undergo coloring in the form of an image, and

2) irradiating the entire expanse of the image-forming agent surface thus obtained including colored parts and yet uncolored parts with long wavelength light radiation which is absorbable by only the colored parts thereby to form a colored image wherein only the colored parts selectively have increased optical densities.

The color of the image in most cases is black, but images of brown or other tones are possible depending on the image-forming agent. These images are herein-

after represented by the term "black image".

By the practice of the image-forming process of this invention, the coloring process step (i.e. the first process step) of coloring in the form of the image, which determines the sensitivity of the finished image-forming material is remarkably simplified, only an extremely small quantity of exposure to ultra violet radiation is sufficient (this quantity differing with the composition but generally being at least 100 mJ/cm² for satisfactory results).

As the succeeding step, the entire expanse of the image-forming agent surface including the primarily colored image parts is irradiated with long wavelength light rays to which the yet uncolored parts are not sensitive, whereupon the image parts only are selectively rendered black. That is, in the second process step, a contrast similar to that due to exposure to image pattern light rays is obtained by merely carrying out entire surface irradiation without resorting to controlled exposure to image-wise light rays. This means that the entire surface irradiation with the long wavelength light rays has not only a mere developing action but also, as an effective result, an effect of increasing the sensitivity of the image-forming agent. The second process step can be completely separated from the first process step.

In accordance with this invention, furthermore, the material of the substrate is not limited, and after the image-forming material has been once formed, it is possible to operate the entire image-forming process without any wet treatment, whereby a black image of excellent resolution can be advantageously obtained.

In a conventional photosensitive material comprising a substrate and an image-forming agent layer of a substance such as a polyacid or molybdenum or tungsten provided as a layer on at least one surface of the substrate, color-change of the image-forming agent is caused by the absorption of a considerable quantity of heat, irrespective of whether it is applied in one stage or whether it is applied in two stages. For this reason, this absorbed heat gives rise to undesirable results such as the occurrence of cracks and pin holes in the surface of the image-forming agent layer, pulverization of the layer, and spreading by oozing of the black parts into the non-image parts. These defects give rise to a lowering of the resolution of the image and a lowering of the preservability or durability of the image, and it is desirable that they be eliminated for practical purposes.

We have found that, by providing the film of the transparent polymer substance

on the image-forming agent layer, all of these defects can be eliminated, and, moreover, the preservation stability of the finished photosensitive or image forming material itself is also improved.

The nature, utility, and further features of this invention will be more clearly apparent from the following detailed description, beginning with a consideration of general aspects and details of the invention and concluding with specific examples of practice illustrating preferred embodiments of the invention.

In the drawings:

FIG. 1 is a fragmentary, enlarged sectional view showing an example of a photosensitive material according to this invention;

FIGS. 2 and 3 are similar sectional views for a description of image formation according to the two-stage process of this invention.

The image-forming process of this invention can be practised through the use of an image-forming photosensitive material having a construction basically as shown in FIG. 1. This material comprises a substrate 1 and an image-forming agent layer 2, which may contain, in addition to the image-forming agent, a binder and/or a reducing agent. A transparent polymer film 3 is provided on the outer surface of the image-forming agent layer 2. The polymer film 3 may also contain a reducing agent, but a reducing agent must be contained in at least one of the image-forming agent layer 2 and the transparent polymer film 3.

The substrate 1 may be of any suitable material such as paper, plastic sheet, glass or metal and be of any suitable shape provided that it has at least one surface.

The image-forming agent used in this invention is one or more polyacids (isopolyacids and heteropolyacids) of molybdenum and tungsten and salts (preferably alkali metal salts and ammonium salts), and complexes of these acids can be used. Specific examples of these suitable image-forming agents are molybdic acid, sodium molybdate, ammonium molybdate, phosphomolybdic acid, ammonium phosphomolybdate, silicomolybdic acid, ammonium silicomolybdate, arsenomolybdic acid, ammonium arsenomolybdate, sodium arsenomolybdate, tungstic acid, ammonium tungstate, phosphotungstic acid, ammonium phosphotungstate, silicotungstic acid, ammonium silicotungstate, sodium silicotungstate, arsenotungstic acid, ammonium arsenotungstate, and sodium arsenotungstate.

In addition, compounds such as complexes with amines such as isopropylammonium molybdate and complexes with other metals such as phosphovanado-

molybdic acid can also be used.

While the above mentioned molybdic acid, tungstic acid, and salts thereof are required to be used in the polyacid form i.e. not including the ortho-acid (monomeric) form and salts thereof, the ortho-acid and salts thereof can be used as a starting material since they exist as an isopolyacid or a salt thereof in an acidic condition.

Ordinarily, an image-forming agent of this character is applied as coating as an aqueous or alcohol solution together with a binder or additionally with a reducing agent as described hereinafter on the substrate 1, and, after drying thereof, the image-forming layer 2 is formed. Accordingly, a polymer compound which is soluble in water or an alcohol such as, for example, gelatin, polyvinyl alcohol, polyvinyl butyral, and cellulose esters are preferably used for the binder. However, other film-forming polymers are capable of being applied as coating in a dispersed state in the presence of a suitable emulsifier.

In addition to water and alcohols, solvents which are capable of dissolving the image-forming agent, such as acetone, methyl ethyl ketone, and dimethylformamide, can be used.

Examples of reducing agents which can be used according to this invention are organic compounds such as D-glucose, thiourea, axalato iron, Micheler's ketone, L-ascorbic acid, diphenylamine, diphenylcarbazide, and polymers such as polyvinyl alcohol, polyvinyl acetate, and polyvinyl butyral; and inorganic compounds such as titanium oxide, zinc oxide, tin chloride, and metals such as lead, tin, iron, and zinc. The reducing agent, however, is not limited to the above enumerated compounds but may be any suitable substance provided that it exhibits a reducing effect with respect to the above described image-forming agent.

Of these reducing agents, those of weak reducing capability such as D-glucose and polymers do not give rise to coloring by merely coexisting with the image-forming agent. Accordingly, these reducing agents can be left in mixed state in the image-forming layer 2. Furthermore, these polymer compounds can possess additionally the effect of the above mentioned binder.

Of the polymers, those such as nitrocellulose do not, themselves, have a reducing effect while they may be used as a binder. With respect to a specific polymer, the determination of whether or not it possesses the desired reducing effect can be made in the following manner. A film (of a thickness of approximately 10 micron) obtained with a weight ratio of 1 of the test substance to 2 of phospho-

molybdic acid is provided on a polyester film which is of non-reducing character and is irradiated for 1 hour with ultraviolet rays from a distance of 20 cm. by a 25-watt mercury lamp. In the case where the difference of the Macbeth optical diffusion transmission densities of the film before and after the irradiation exceeds 0.01, this test substance can be used as a reducing agent according to this invention.

On the other hand, when strongly reducing substances such as thiourea, oxalato iron, L-ascorbic acid, diphenylamine, diphenylcarbazine, and Micheler's ketone are caused to be contained in the image-forming layer 2, they become a cause of fogging. Accordingly, when these strongly reducing substances are to be contained in the image-forming material structure, it is preferable that they be contained in the polymer film (hereinafter referred to as "over-coat layer") 3.

For the polymer to be used for forming the over-coat layer 3 in the improved image-forming material, any material which is transparent and can be applied as a coating can be used. In the case where a polymer which is soluble in water or an alcohol is used as a binder of the image-forming layer 2, it is desirable that a polymer which is insoluble in water or an alcohol be used for this over-coat layer forming polymer. The reason for this is to prevent dissolution of the image-forming layer 2 once formed and disturbance of the interface between the image forming layer 2 and the over-coat layer 3 in the application of the over-coat layer forming polymer in the form of a solution. In many cases, the image is formed in the image-forming layer 2 in the vicinity of the interface between it and the over-coat layer 3, and the prevention of disturbance of the interface is important for increasing the resolving power.

A further reason is that when a solvent capable of dissolving the image-forming layer is used for the purpose of forming the over-coat layer, and a strong reducing agent is contained in this solution, dissolving of the image-forming occurs and, simultaneously, coloring is caused upon application of the solution on the image-forming layer. Examples of preferred over-coat layer forming polymers are polyvinyl chloride resins, polyvinyl acetate resins, polyvinylidene chloride resins, cellulose resins, polystyrene, polypropylene, polyvinyl carbazole, polymethacrylate resins, polyamide resins, polyurethane resins, fluorine resins, and rubber chlorides. Polyvinyl chloride resins and polyvinylidene chloride resins function also as reducing agents.

A representative process for producing

image-forming materials on the basis of the above described starting material will now be described.

First, the image-forming agent is dissolved in water or an alcohol, and, depending on the necessity, a binder and/or a weak reducing agent are/is further dissolved in the solvent. The solution thus obtained is applied as a coating on the substrate 1 and dried in air thereby to form the image-forming layer 2.

In the case where a paper possessing absorptivity is used for the substrate 1, it can function additionally to have a reducing effect (through metal oxid pigments and polymeric sizing agents) and the effect of a binder. For this reason, the combined structure of the substrate 1 and the image-forming layer 2 of this invention can be produced by applying image-forming agent directly without using an additional binder and/or reducing agent.

However, the use of a binder in the solution of the above mentioned image-forming agent is preferable for image formation and for coating characteristic of the solution. When a binder is used, it is preferable that its concentration be such that the image-forming agent concentration in the image-forming layer in the dry state will be greater than 15 percent by weight in order to impart a high optical density to the image. Furthermore, it is preferable, in order to maintain the film characteristic of the image-forming layer in a good state, that the concentration of the binder in the dry state be 10 to 60 percent by weight.

When the image-forming layer 2 is to contain a reducing agent, the quantity in which it is used depends on the reducing power of the reducing agent, but adjustment wherein this quantity is made small for a relatively strong reducing agent and is made somewhat on the greater side for a relatively weak reducing agent is necessary. In any case, the appropriate quantity of the reducing agent is determined within a range wherein the image-forming layer does not undergo substantial coloring when irradiated with light rays not containing ultraviolet rays.

For example, when D-glucose, which is a relatively weak reducing agent, is used in combination with a phosphomolybdic acid, image-forming agent, a D-glucose concentration in the image-forming layer in dry state of 5 to 50 percent by weight is suitable.

Furthermore, when the reducing agent functions additionally as a binder as in the case of the above mentioned polymer reducing agents, the above set forth concentration range of the binder can be applied directly as it is.

A thickness of the image-forming layer 2 on the substrate 1 of 2 to 20 microns is desirable. When this thickness is less than 2 microns, the image density is slightly deficient. On the other hand, when this thickness exceeds 20 microns, the density prior to exposure to light (therefore the density of the non-image parts) increases, and, for this reason, there is a tendency of the contrast of the image to become poor.

To form the over-coat layer 3, the over-coat layer forming polymer is dissolved preferably in a solvent which will not dissolve the image-forming agent and the binder. For example, in the case where a binder which is soluble in water and alcohols is used in the image-forming layer, the over-coat layer forming polymer is dissolved in an organic solvent of relatively low solubility in water and alcohols such as, for example, benzene, toluene, and tetrahydrofuran, and, depending on the necessity, a reducing agent is additionally admixed, and the resulting mixture is applied as a coating on the image-forming layer 2. In the case where the reducing agent in this process is insoluble in the solvent, the reducing agent is rendered into fine powder and dispersed in the binder solution by the use of means such as an ultrasonic dispersion machine, and then the resulting dispersion is applied as a coating on the image-forming layer 2. The solvent is then evaporated off by drying in a stream of air, whereupon the over-coat layer 3 is obtained.

We have found that a thickness of the over-coat layer 3 of 5 to 15 microns is desirable. With a thickness less than 5 microns, the effect from the image part cannot be neglected, and the effectiveness of the over-coat is deficient. On the other hand, when the thickness exceeds 15 microns, the light absorbing efficiency of the image-forming layer 2 becomes poor, and the sensitivity of the structure as a photosensitive material tends to decrease.

For the application of the solution or dispersion of the above described image-forming agent on the substrate or the over-coat layer forming agent, any of the conventional methods such as bar coating, roll coating, wheeler coating, dip coating, and spray coating can be used.

The image-forming material of the invention produced in the above described manner can assume the following three dispositions of the reducing agent depending on its presence in the image-forming layer 2 and the over-coat layer 3.

- a). The case where the reducing agent is contained in the over-coat layer 3.
- b). The case where the reducing agent is contained in the image-forming layer 2.
- c). The case where the reducing agent is

contained in both the over-coat layer 3 and the image-forming layer 2.

In each of the above three cases, the image-forming material of the invention fully exhibits the aforementioned highly desirable characteristics. That is the occurrences of various defects such as cracks and pin holes in the surface of the image-forming layer 2, pulverization of the surface, and oozing of the image parts into the non-image parts are effectively eliminated, and other effects such as an improvement in the resolution of the image and the preservability of the image and an improvement in the preservation stability prior to use are attained.

However, differences are observed on the following points. The above case b) corresponds to a structure wherein an over-coat layer is provided on an image-forming layer of a conventional photosensitive material, but, for equal reducing power of the reducing agent, the sensitivity in the case a) is slightly lower than that in this case b). However, the case a) is advantageous in that a strong reducing agent can be used therein and is superior in preventing fogging. In this case, furthermore there is a great advantage in that, by forming an over-coat layer containing the reducing agent a short time before the use of the photosensitive material, the preservability of the image-forming material can be remarkably improved. On one hand, the sensitivity in the case c) rises to approximately twice that in the case b).

The image-forming process of this invention with the use of the image-forming material obtained in this manner will now be described. This process comprises two process steps.

In the first step, the image-forming agent layer 2 provided on the substrate 1 is reduced image-wise thereby to obtain coloring parts. In the coating of the image-forming agent layer 2 on the substrate 1, the reducing agent is caused to coexist (inclusive of both the cases where the reducing agent is contained in the image-forming agent layer 2 and the case where it is contained in the over-coat layer 3), and the surface of the image-forming layer 2 on the support 1 thus obtained is irradiated with image-wise ultraviolet radiation through the over-coat layer 3 of the photosensitive material onto the outer surface of the image-forming layer 2 (or the interface between the layer 2 and the over-coat layer 3, which interface or the outer surface will hereinafter be referred to as "image-forming surface"), as shown in Fig. 2. With an irradiation energy of 100 mJ/cm², a primary coloring part of light blue color of the image pattern is obtained on the image-forming surface.

The term "ultraviolet radiation" is used herein to designate light radiation which include light of the wavelength of the ultraviolet region, and which may include additionally visible light and infrared light. For the light source to emit the image-wise ultraviolet radiation, a mercury lamp, a xenon flash, a laser beam, and other sources can be used. By passing these ultraviolet radiation through a transmission original 5, image-wise ultraviolet radiation can be obtained. Laser light can be projected image-wise as a direct beam. Furthermore, ordinary camera photography is also possible, but in this case, of course, it is necessary that the irradiation light to be projected onto the objective be ultraviolet radiation.

Then, in the second process step, the entire image-forming surface including the colored parts and yet uncolored parts obtained in the above described manner is irradiated with light radiation of long wavelength which cannot be sensed by the yet uncolored parts thereby to render only the above mentioned colored parts selectively into black or dark color and thereby to obtain the image part 6, as shown in Fig. 3.

It is necessary that the above mentioned long wavelength light radiation be those which result after light radiation of short wavelengths such as to be absorbed by the yet uncolored parts are selectively cut off. The critical wavelength satisfying the conditions of being absorbed only by the colored parts and not being absorbed by the yet uncolored parts differs with the various combinations of the image-forming agent and the reducing agent, but it has been found that, generally, this critical wavelength is in the vicinity of the boundary between the visible light region and the ultraviolet light region. This long wavelength light can be obtained by passing the light from a light source such as xenon lamp, a tungsten lamp, a xenon flash, or a laser device through a filter cutting off ultraviolet radiation.

By the irradiation at this stage, the densities of the colored parts increase with increase in the quantity of light absorbed by these parts, which thus reach colors close to jet black, but the non-colored parts undergoing almost no variation. Accordingly, the exposure at this stage can be selected within any range in accordance with the required contrast, but even with an exposure of minimum of 2.5 J/cm^2 , a satisfactory contrast can be obtained.

The black image thus obtained has a contrast of a degree of clarity which could not be attained with a conventional non-silver photosensitive material. Even when it is left naturally, this material exhibits

semipermanency in undergoing no color change, and the non-image parts also do not assume a black color. However, in order to leave an image which is stable with respect to even heating and ultraviolet light, it is preferable to carry out fixing treatment. More specifically, in accordance with this invention, the uncolored image-forming agent remaining in the non-image parts can be caused to lose its image-forming capability by treating it with an alkaline substance such as ammonia gas, ammonia water, or an aqueous solution of sodium hydroxide. As a result, an image which has been subjected to this alkali treatment has a high contrast, and the material is characterized in that the non-image parts is not caused to change color even by heating.

Another noteworthy feature is that this alkali treatment is effective not only after the formation of the black image but also when applied to the entire surface of the image-forming agent after the primary coloring. More specifically, when the surface of the image-forming agent after the primary coloring is treated with a suitable concentration of alkali for a suitable time (e.g. 2-3 secs. in NH_3 gas), the uncolored parts lose their image-forming capability, but the image parts which have once been colored do not lose their capability of turning black and are selectively rendered black by irradiation with long wavelength light radiation.

The above described image-forming process and material according to this invention can be advantageously applied to systems such as rapid reproduction systems, projection image preparing systems, and IC mask material preparing systems. By such application the operational characteristics of these systems are remarkably improved because of advantages such as high image density, high resolving power and sensitivity, and good preservation stability of the image-forming material prior to and after exposure.

In order to indicate more fully the nature and utility of this invention, the following examples of practice constituting preferred embodiments of the invention are set forth, it being understood that these examples are present as illustrative only and that they are not intended to limit the scope of the invention. Throughout the following examples, quantities expressed in "parts" and "percent" (%) are by weight.

Example 1.

One part of phosphomolybdic acid was dissolved in 5 parts of a 10-percent aqueous solution of polyvinyl alcohol, and the resulting solution was applied as a coating on a sheet of polyester film with a wire

bar and then dried for 5 minutes in an oven at 50°C, whereupon an image-forming layer was obtained. Then, as an over-coat layer, a 5-percent toluene solution of polyvinyl chloride was applied as a coating on this image-forming layer with a wire bar and then dried for 5 minutes in an oven at 50°C. As a result, a photosensitive structure of a thickness of 13 microns (image-forming layer approximately 8 microns, over-coat layer approximately 5 microns).

A transmission original was placed in direct contact with this photosensitive structure, which was then exposed for 10 seconds to light from a 500-watt ultrahigh-voltage mercury lamp at a distance of 30 cm., whereupon an image wherein the exposed parts had become blue. The transmission original was removed, and the entire surface of the photosensitive structure thus exposed was exposed to light from a xenon flash lamp (RISO TRANPEN' UP TU-207) having passed through a filter for cutting off ultraviolet rays ("Toshiba" AT-V-Y 47—"Toshiba" is a Registered Trade Mark). As a result, an image wherein only the blue parts of the image exposed to the ultrahigh-voltage, mercury-arc lamp had become black was obtained.

It was found that the optical transmission density of the image parts had increased remarkably, from a density of 0.1 prior to flash exposure to a value of 2.0 after flash exposure. During this period, the transmission density of the non-image parts remained at 0.04.

Example 2.

One part of phosphomolybdic acid was dissolved in 5 parts of a 10-percent polyvinyl butyral alcohol solution. The resulting solution was applied as a coating layer on a sheet of art paper with a wire bar and then dried for 5 minutes in an oven at 50°C, whereupon an image-forming layer was obtained on the art paper. On this image-forming layer, a 10-percent toluene solution of ethylcellulose was applied as an over-coat layer thereby to produce a photosensitive structure. By using this photosensitive structure, the procedure set forth in Example 1 was followed, whereupon a black image was produced.

Example 3.

One part of phosphomolybdic acid was dissolved and dispersed in 5 parts of a collodion solution, and the resulting solution was applied by dip coating onto a glass substrate to obtain an image-forming layer. Onto this image-forming layer, a 5-percent polyvinylidene chloride/tetrahydrofuran solution was applied as a coating layer and dried for 5 minutes in an oven at 50°C to produce a photosensitive struc-

ture. With the use of this photosensitive structure a black image was obtained by the process set forth in Example 1.

Example 4.

A photosensitive structure obtained as in Example 1 except for the use of silicomolybdic acid instead of phosphomolybdic acid was used similarly as in Example 1 to produce a black image.

Example 5.

A photosensitive structure obtained as in Example 2 except for the use of silicomolybdic acid instead of phosphomolybdic acid was used similarly as in Example 2 to produce a black image.

Example 6.

A photosensitive structure obtained as in Example 3 except for the use of silicomolybdic acid instead of phosphomolybdic acid was used similarly as in Example 3 to produce a black image.

Example 7.

One part of phosphotungstic acid was dissolved in 5 parts of a 10-percent polyvinyl butyral alcohol solution, and the resulting solution was applied as a coating layer on a sheet of art paper with a wire bar thereby to produce an image-forming layer. A 5-percent vinyl chloride resin solution in toluene was applied on this image-forming layer, whereupon a photosensitive structure was obtained. This photosensitive structure was exposed to light from a xenon flash lamp (RISO TRAPEN' UP TU-207, manufactured by Riso Kagaku Sha, Japan) having passed through a filter for cutting off visible and infrared rays and through a transmission original placed in direct contact with the surface of the photosensitive structure. As a result, an image wherein the light-exposed parts were colored was obtained.

The transmission original was then removed, and the entire surface of this photosensitive structure thus light-exposed was exposed to light from a xenon flash lamp passed through a filter for cutting off ultraviolet rays, whereupon an image wherein blue parts had blackened was obtained.

Example 8.

One part of a substance obtained from a reaction of isopropylamine and phosphomolybdic acid was dissolved in 5 parts of a 10-percent polyvinyl butyral alcohol solution, and the resulting solution was applied as a coating on a polyester film with a wire bar, whereupon an image-forming layer was obtained. A 5-percent vinyl chloride resin/tetrahydrofuran solution was then applied as a coating on this image-forming layer, whereupon a photosensitive structure was obtained. With the use of this photosensitive structure, a black image was obtained by the procedure set forth

in Example 1.

WHAT WE CLAIM IS:—

1. An image-forming material comprising:
 5 a substrate;
 an image-forming layer provided on or absorbed in at least one surface of the substrate and containing an image-forming agent selected from polyacids of
 10 molybdenum and tungsten and salts and complexes of these polyacids; and
 a transparent polymer film provided on the image-forming layer
 at least one of the image-forming layer
 15 and the transparent polymer film containing a reducing agent capable of reducing the image-forming agent when irradiated with ultra-violet radiation.
2. An image-forming material as claimed
 20 in claim 1 in which the image-forming agent is at least one of molybdic acid, sodium molybdate, ammonium molybdate, phosphomolybdic acid, ammonium phosphomolybdate, silicomolybdic acid, ammonium silicomolybdate, ammonium arsenomolybdate, tungstic acid, ammonium tungstate, phosphotungstic acid, ammonium phosphotungstate, silicotungstate, arsenotungstic acid, ammonium arsenotungstate,
 25 sodium arsenotungstate, isopropylammonium molybdate, and phosphovanadomolybdic acid.
3. An image-forming material as claimed
 in claim 1 or 2 in which the reducing agent
 35 is selected from D-glucose, thiourea, oxalato-iron, Michler's ketone, L-ascorbic acid, diphenylamine, diphenyl-carbazide, titanium oxide, zinc oxide, tin oxide, lead, tin, iron, zinc and reducing polymer compounds, each of said reducing polymer compounds being characterized in that when
 40 a mixture of one part by weight thereof with two parts by weight of phosphomolybdic acid is applied as a film on a
 45 polyester film which is non-reducing and irradiated for one hour by a 250-watt mercury lamp from a distance of 20 cm., the difference between the values of the MacBeth optical diffusion transmission density
 50 respectively before and after irradiation becomes greater than 0.01.
4. An image-forming material as claimed
 in Claim 3 in which the image-forming
 55 agent layer contains a weak reducing agent selected from D-glucose and the reducing polymer compounds.
5. An image-forming material as claimed
 in any one of claims 1 to 4 in which the
 60 image-forming agent layer further contains a binder.
6. An image-forming material as claimed
 in claim 5 in which the binder is a polymer
 compound soluble in water or an alcohol,
 and the polymer compound forming the
 transparent polymer film is insoluble in 65
 water or an alcohol.
7. An image-forming material as claimed
 in any one of claims 1 to 4 in which
 the image-forming agent layer contains a
 reducing polymer compound as a reducing 70
 agent and, additionally, as a binder.
8. An image-forming material as claimed
 in claim 7 in which the reducing polymer
 compound is selected from polyvinyl alcohol,
 polyvinyl acetate and polyvinyl butyral. 75
9. An image-forming material as claimed
 in any one of claim 1 to 8 in which the
 polymer compound constituting the transparent
 polymer film is selected from polyvinyl
 chloride, polyvinyl acetate, poly- 80
 vinylidene chloride, cellulose resins, polystyrene, polypropylene, polyvinyl carbazole,
 polymethacrylate resins, polyamide resins,
 fluorine resins, and rubber chloride.
10. An image-forming material as 85
 claimed in any one of claims 1 to 9 in
 which the concentration of the image-forming
 agent in the image-forming layer
 is greater than 15 percent by weight.
11. An image-forming material as 90
 claimed in any one of claims 1 to 10 in
 which the thickness of the image-forming
 layer is 2 to 20 microns, and the thickness
 of the polymer film is 5 to 15 microns.
12. An image-forming material as 95
 claimed in claim 1 substantially as described
 in any one of the Examples.
13. An image-forming material as
 claimed in claim 1 substantially as described
 herein with reference to and as 100
 illustrated by Figure 1 of the accompanying
 drawing.
14. An image-forming process which
 comprises:
 1) subjecting an image-forming material as 105
 claimed in any one of claims 1 to 13 to
 image-wise exposure to ultra-violet radiation
 to cause reduction of the image forming
 agent and to cause it to undergo coloring
 in the form of an image, and 110
 2) irradiating the entire expanse of the
 image-forming agent surface thus obtained
 including colored parts and yet uncolored
 parts with long wavelength light radiation
 which is absorbable by only the colored 115
 parts thereby to form a colored image
 wherein only the colored parts selectively
 have increased optical densities.
15. An image-forming process as claimed
 in claim 14 further comprising a process 120

step wherein residual image-forming agent remaining in non-image parts are contacted with an alkaline substance and thereby caused to lose image-forming capability.

5 16. An image-forming process as claimed in claim 14 or 15 in which the image-forming agent surface is irradiated with not less than 100 mJ/cm² of ultraviolet radiation.

10 17. An image-forming process as claimed in claim 14, 15, or 16 in which the image-forming agent surface after the coloring is irradiated with not less than 2.5 J/cm² of long wavelength light radiation.

15 18. An image-forming process as claimed in claim 14 substantially as described here-

in with reference to and as illustrated in Figures 2 and 3 of the accompanying drawings.

19. An image-forming process as claimed 20 in claim 14 substantially as described in any one of the Examples.

20. An imaged substrate obtained by a process as claimed in any one of claims 14 to 19.

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FIG. 1



FIG. 2

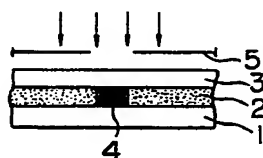


FIG. 3

